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The Photocatalytic Applications of TiO_2-WO_3 Heterostructure in Methylene Blue

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Abstract

In this work, TiO_2-WO_3 composite materials were forged by sol-gel method and the forged samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy and UV-vis diffuse reflectance spectroscopy. The tough interaction in the interface of TiO_2-WO_3 heterostructures and the solar spectral response of TiO_2 and WO_3 reduce the electron-hole pair recombination rate and enhance the photoelectrochemical activity. The TiO_2-WO_3 heterostructures also show good adsorption ability for organic pollutants. This study testified that the fabricated TiO_2-WO_3 heterostructures are expectation materials for efficient water splitting as well as adsorption and photocatalytic wipe off organic pollutants.

***Keywords*:** titania dioxide; tungsten trioxide; photocatalytic; methylene blue.

1. Introduction

In recent years, photocatalysis technology has received widespread attention on account of its applications in organic synthesis and the abatement of pollutants in water and air [1]. It is applied to wipe off the organic pollutant which includes detergent,dyes,pesticides and herbicides under UV-light irradiation.The heterogeneous photocatalyst attracted a crucial attention due to elimination of organic pollutants in water[2-5] and semiconductor photocatalysts drew attention because of inexpensive and environmental friendliness.

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Photocatalysis is used to eliminate pollutants by conversion of optical energy into the electrochemical energy required for photo-oxidation by a catalyst[6].Titanium dioxide (TiO_2) is demonstrably the most promising material for applications to air and water purification from various pollutants [7]. However, TiO_2 only works in conjunction with irradiation of limited wavelength: TiO_2 band gap (Eg≈3.2 eV) requires λ<385 nm, which rules out 95% of the solar spectrum.Moreover, the rapid recombination of the photocatalytically produced charge carriers competes with the electron transfer of the reactants adsorbed on the catalyst surface,which makes it not fit for efficient utilization[8].A arge number of methods have been used to increase the photocatalytic property of TiO_2 for instance doping with metal or metal oxides, noble metal deposition and anion doping etc. Among semiconductor oxides, crystalline tungsten oxide (WO_3) has some advantages including: induction of surface acidity to promote adsorption of OH^-; water and pollutant molecules ;its band gap is short (2.6-2.8 eV), thus requiring longer wavelengths for the excitation [9]. The lower conduction band (CB) position of WO_3 than that of TiO_2 accelerates the electron transfer from TiO_2 to WO_3 and the holes transfer in opposite direction. The idea of coupling TiO_2 with another metal oxide with appropriate band gap and edge positions can be used as a feasible channel to promote photoproduced charge separation. Pandi and Gopinathan[10]fabricated TiO_2/WO_3 synthetic material by hydrothermal synthesis and surface modification. The enhanced decomposition of aqueous eosin-Y with TiO_2/WO_3 was because of visible light absorption and decreased carrier recombination rate. Ke etal.[11]fabricated TiO_2/WO_3 synthetic material hydrothermally with CTAB as a surfactant.The TiO_2/WO_3 disintegrated 100% of RhB in 50 min. Riboni and his colleagues [12]prepared WO3-TiO2 mixed oxide by a sol-gel method. The photocatalyst with the optimum tungsten content of 3% had higher activity than TiO2 P25 and degraded 31% acetaldehyde in2 h in the gas phase under mainly visible irradiation. Similarly, Eibl and his colleagues [13]state that WO_3 is formed in tungstated titania when the tungsten loading exceeds a mass fraction of 20% and the powders are calcined above 923 K. In summary, the literature has inadequately characterized the TiO_2/WO_3 semiconductor catalyst. In this work,we fabricated WO_3 by hydrothermal method and fabricated TiO_2、 TiO_2-WO_3.The fabricated samples were characterized by various techniques for example X-ray diffraction(XRD), X-ray photoelectron spectroscopy (XPS),scanning electron microscope (FESEM) and UV-vis diffuse reflectance (UV-Vis-DRS) spectroscopy.The prepared TiO_2-WO_3 heterostructures have predominant interfacial interactions with tunable electrical property and show better photocatalytic activity. The TiO_2-WO_3 hetero structures also show good degradation competence towards the organic pollutant,methylene blue (MB).

2. Materials and Methods

2.1. Chemicals

Ammonium tungsten partial, Ammonium metatungstate hydrate (AMT); Tetrabutyl titanate(TBOT);ethyl alcohol absolute(C_2H_6O);hydrochloric acid(HCl); AceticAcid(CH_3COOH) ; methylene blue(MB);All chemicals and reagents were of analytical grade and were used as such without further purification, and double distilled water was used throughout this work.

2.2. Catalyst preparation

Tungsten trioxide (WO_3) powder was prepared by hydrothermal method.Weigh ammonium metatungstate

(AMT) and add it to 20mL of deionized water, stirring constantly until dissolved.Then add hydrochloric acid to the resulting solution to adjust the pH to 2.After stirring the solution for half an hour, transfer the solution to a 100 mL high-pressure reactor, put the high-pressure reactor into a drying oven, and keep the oven at 180℃ for 24 hours. After cooling the reactor to room temperature, take out the product and centrifuge and wash the product.First wash with deionized water for three times and then wash with anhydrous ethanol for three times. Then dry at 80℃, grind the dried products to obtain pale yellow powder products. TiO_2 powder was prepared by sol-gel method.Tetrabutyl titanate was added into anhydrous ethanol and stirred for 20 min to obtain yellow clarification solution A.Deionized water and glacial acetic acid were added into anhydrous ethanol, and proper amount of nitric acid was added after full stirring. PH value was adjusted to 2 to obtain solution B.Then under the intense mixing, mixing solution A and solution B, fully mixing stand for 24 hours, after get the gel after place into the oven, drying under 80℃ temperature, then put the samples in under 550 ℃ heat treatment resistance furnace, heating speed 2℃ per minute, after the heat treatment of samples of grinding end up with white powder.

2.3. Photocatalytic activity

Photocatalytic activity test was performed as follows. 0.3g $WO_3/TiO_2/WO_3$-TiO_2 composites were added to 300 mL MB (300 mg/L) aqueous solution and the suspension solution was stirred in the dark for 30 min until the adsorption/desorption process reached equilibrium. Xe lamp was employed as the UV-visible light source, and it was placed 14 cm away from the solution. In every 20 min, 5 mL of the solution was taken away and the suspension was removed by using centrifugation. Then measuring the maximum absorbance at 665 nm of the MB by the spectrophotometry.The degradation rate was calculated using $E=(1-C/C_0)$, where C_0 and C are the MB concentrations before and after photodegradation with UV-visible light.

3. Results and discussion

Control TiO_2 phase (**Figure.1a**) is pure anatase with a tetragonal structure (JCPDS＃01-083-0950). Control WO_3 (**Figure.1b**) exhibits main peaks indexed as monoclinic crystalline structure (JCPDS＃01-083-0950). In the TiO_2 sample the diffraction peak of [101] at$2\theta = 25.28°$ and the peak of [200] of WO_3 at $2\theta = 24.36°$ are the highest intense, show that [101,200] are the most growth orientations.As evident from the XRD patterns (**Figure.1c**) the main anatase peaks [101,103,200,105,213] at $2\theta = 25.3°$,37.9° ,48.4° ,53.9° ,62.7° and the monoclinic form peaks [200,220,222,400,420,422] at 2θ =23.6°，33.6°，41.5°，48.4°，54.6°，60.3°.Besides, no phase transformation of TiO_2 or of WO_3 occurred during the compound of the hybrid powders: in all the samples TiO_2 maintained the anatase structure, while WO_3 kept the monoclinic form.

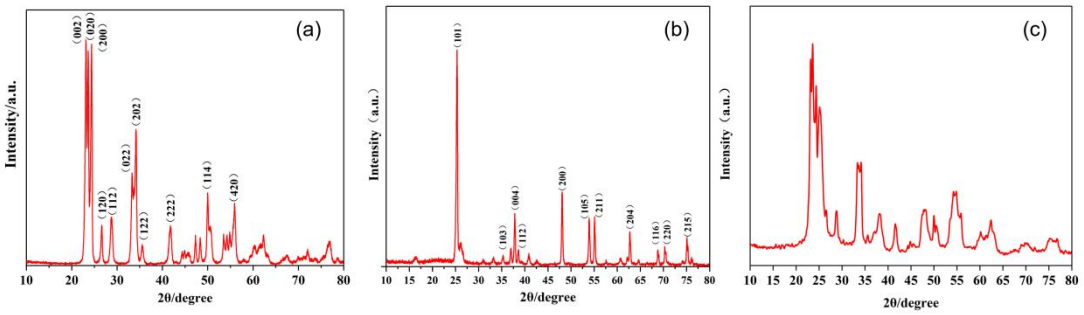

Figure 1: (a) XRD patterns of WO_3 (b) XRD patterns of TiO_2, (c) XRD patterns of TiO_2-WO_3 heterostructures.

We report the field emission scanning electron microscope (SEM) micrographs of control TiO_2 and WO_3 and hybrid TiO_2-WO_3 powders calcined at 550 °C **Figure. 2**.

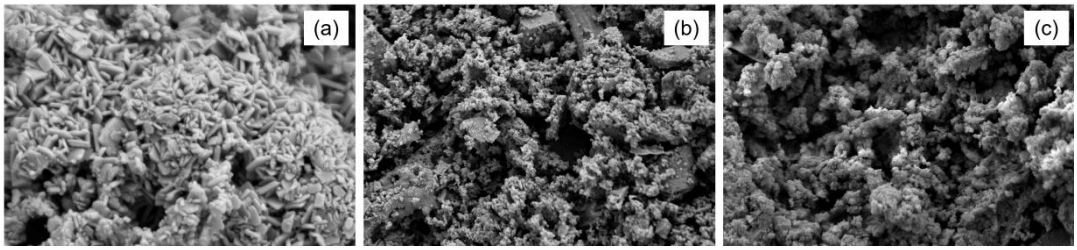

Figure 2: (a) SEM images of WO_3 (b) SEM images of TiO_2 (c) SEM images of TiO_2-WO_3 heterostructures.

X-ray photoelectron spectroscopy (XPS) was applied to further research the chemical and bonding environment of the composite powders.**Figure.3 a** presents a low-resolution full range XPS spectrum of the TiO_2-WO_3 composite powders. The XPS survey spectrum showed that the distinctive as well as the Auger peaks of Ti, O, W and the combined material confirmed the presence of titanium, oxygen, tungsten . The Ti2p high resolution XPS spectra are analyzed in **Figure.3 b**. The binding energies of 459.6 and 465.25 eV are state that $Ti2p_{3/2}$ and $Ti2p_{1/2}$ separately. The splitting of the 2p doublet was 5.65 eV, reveal a normal state of Ti^{4+} in the TiO_2-WO_3 composite powders.The high-resolution W4f XPS (**Figure.3 c**) shows the peaks at 38.4 and 36.3 eV corresponding to the characteristic $W4f_{5/2}$ and $W4f_{7/2}$ components respectively in WO_3. The energy gap between these two peaks is 2.1 eV which suggested the W^{6+} oxidation state in WO_3.The XPS results confirm the superior interaction between TiO_2 and WO_3 through the formation of Ti-O-W bonds in TiO_2-WO_3 heterostructures.With respect to the XPS spectra of O1s in **Figure.3 d**,the O1s peak at 530.95 eV is attributed to O^{2-}.

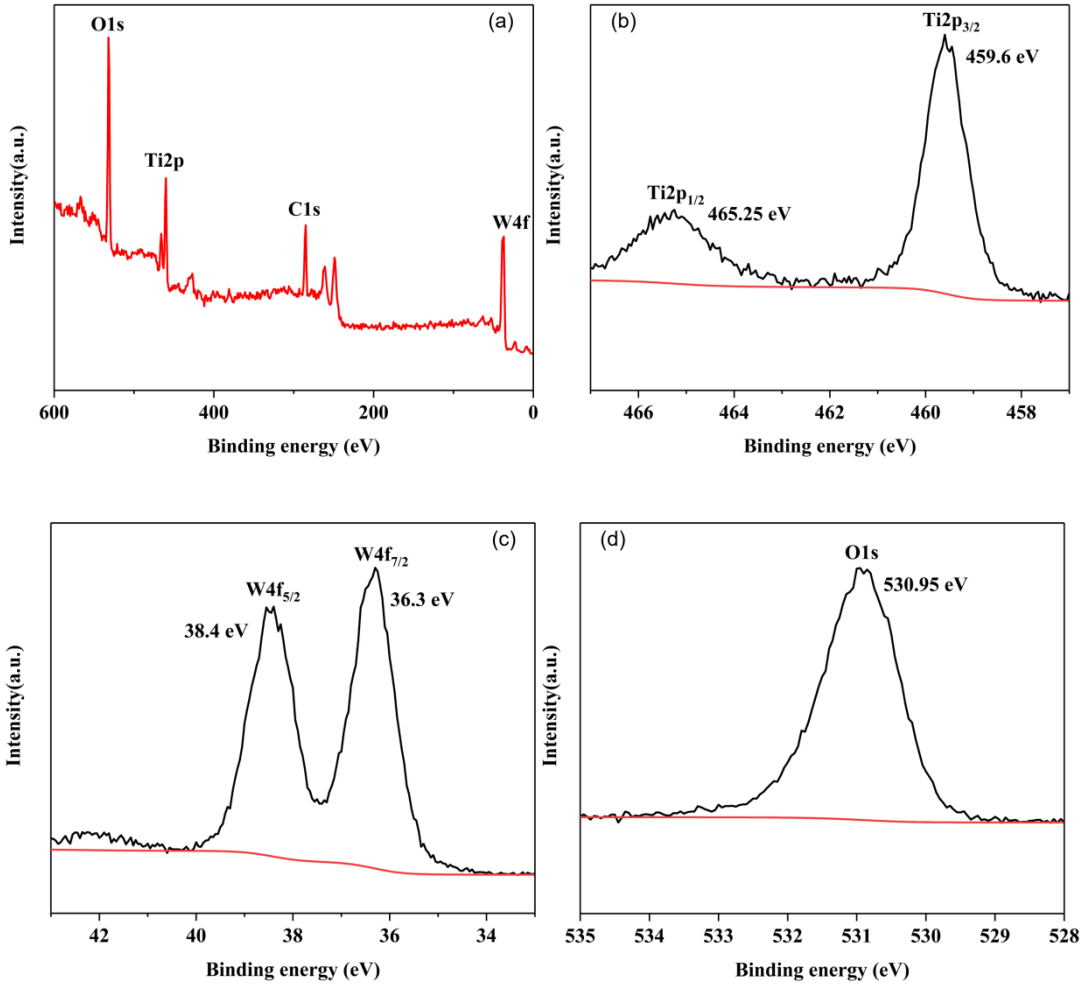

Figure 3: XPS spectra of the TiO_2-WO_3 heterostructures: (a) fully scanned spectra; (b) XPS spectra of Ti2p; (c) XPS spectra of W4f (d) XPS spectra of O1s.

The UV-Vis-DRS spectrum was recorded to understand the light absorption property of the samples and shown in **Figure.4 a**.The re-flectance of TiO_2-WO_3 heterostructures reduced with the addition of WO_3 content which revealed the enhanced absorption of the incident light. We used Tauc diagram to calculate the band gap of the prepared samples.The transformed Kubelka-Munk function, $[F(R)hv]^{1/2}$ ($F(R) = (1-R)^2/2R$ and R is the reflectance) was plotted against the energy of light, hv. The intercepts of the tangent drawn at absorption function to the energy axis at zero absorption are evaluated to get the band gap values[15]. The band gap of TiO_2 and WO_3 was 3.12 eV(**Figure.4 c**) and 2.52 eV(**Figure.4 b**),and the TiO_2-WO_3 heterostructures band gap was 2.36 eV(**Figure.4 d**). The fractionally reduced band gap values in TiO_2-WO_3 heterostructures compared to pure TiO_2 shows the hard interaction between TiO_2 and WO_3. The strong mutual effect can availably hinder the recombination of e^--h^+ through the TiO_2-WO_3 heterojunction.

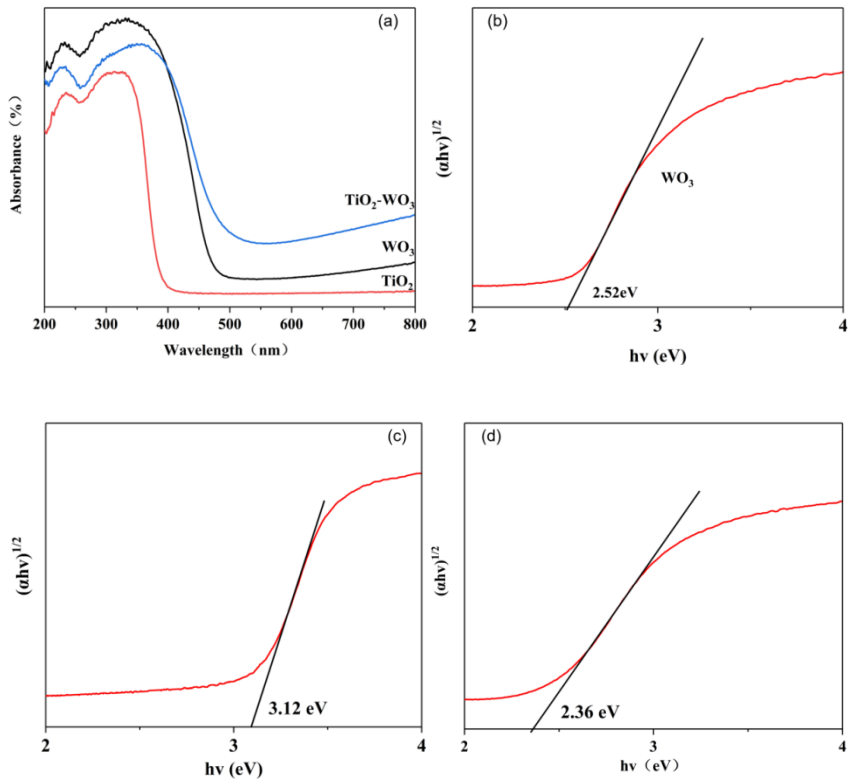

Figure 4: (a) UV-Vis-DRS spectra of TiO_2、$WO_3$and TiO_2-WO_3 (b) (c) (d)Tauc plot of TiO_2、$WO_3$and TiO_2-WO_3 heterostructure.

Figure.5 shows photocatalytic activity of as-prepared TiO_2、WO_3 and TiO_2-WO_3. It can be observed that TiO_2-WO_3 possesses the highest photocatalytic degradation rate (99% within 100 min), which is higher than that of WO_3 (57%) and TiO_2 (25%) at the same condition.

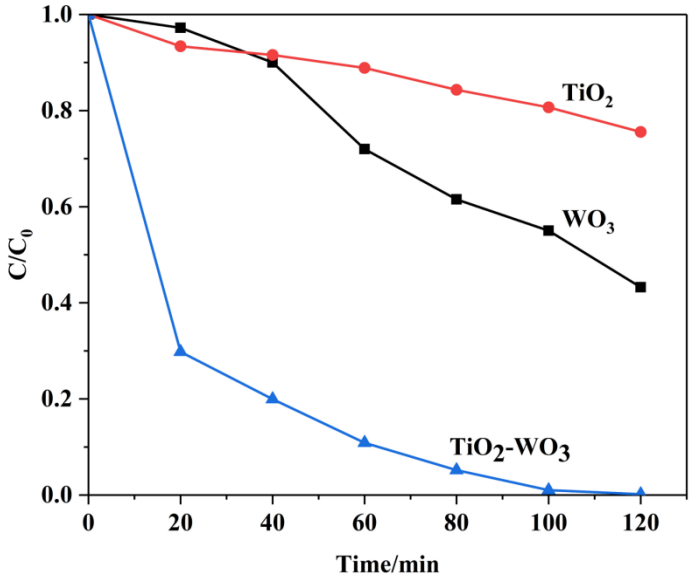

Figure 5: Photodegradation of Methylene blue in the presence of TiO_2、WO_3 and TiO_2-WO_3 composites.

4. Conclusions

A simple sol-gel method followed by calcination process was used to synthesize TiO_2-WO_3 heterostructures with superior interfacial interactions. The TiO_2-WO_3 showed almost complete removal of MB in 100 min under visible light by photocatalytic and adsorption processes suggesting the higher adsorption of MB on the surface of TiO2-WO3 heterostructures.The band gap of TiO_2 reduced from 3.12 eV to 2.36 eV in the TiO_2-WO_3 heterostructures which show the formation of heterojunction, and resulted in the reduction of recombination of e^--h^+ pair.TiO_2 and WO_3 act in synergy: due to the difference in band possible of the semiconductors, electrons shift from the conduction band of TiO_2 to that of WO_3 upon UV light irradiation. This research projects TiO_2-WO_3 heterostructures with great promise solar and visible light active materials for efficient water splitting as well as adsorption and photocatalytic reduce of organic pollutants.

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